Glass and Ceramics *Vol. 66, Nos. 11 – 12, 2009*

UDC 666.266

INVESTIGATION OF THE POSSIBILITY OF REPLACING HIGH-LEAD GLASSES IN FUSIBLE GLASS SOLDERS BY LESS TOXIC GLASSES

D. A. Geodakyan,[1,2] B. V. Petrosyan,[1] S. V. Stepanyan,[1] and K. D. Geodakyan[1]

Translated from *Steklo i Keramika*, No. 11, pp. 15 – 18, November, 2009.

The possibility of partial or complete replacement of PbO in fusible glass solders by less toxic components is investigated. It is found that it is impossible to find a full-fledged replacement for glasses in the lead-borate eutectic, used as the glass base in glass soldering compositions for sealing glass ceramic packages of integrated microcircuits at temperatures 390 – 420°C, within the systems $PbO – P_2O_5 – ZnO – B_2O_3$, $V_2O_5 – P_2O_5 – ZnO – B_2O_3$, and $TeO_2 – PbO – V_2O_5 – Bi_2O_3$ with different additives and total mass content of class-I hazard components not exceeding 70%.

Key words: glass, solder, fusible, electronics, microcircuit.

Integrated microcircuits are ordinarily assembled in metal, plastic, cermet, or glass ceramic packages. The latter have a number of advantages: manufacturability and low cost as compared with cermet packages and mechanical and dielectric properties as compared with plastics and, in part, metal packages. In addition, microcircuits assembled in cermet packages are hermetic, reliable, and long-lasting.

The technical-operational characteristics of the cermet packages of integrated microcircuits are largely determined by the properties of the glass solders used to glue the ceramic parts and the metal leads of the microcircuits in a hermetic case. In this connection the glass solder must form a mechanically strong and chemically stable vacuum-tight dielectric layer between the parts of the package and the leads of the microcircuits at a prescribed temperature.

The main characteristics of the glass solders are the volume resistivity ρ, permittivity ε, CLTE, and sealing temperature. The higher ρ and the lower ε of the glass solder, the more the leads can be placed per unit surface area of a package and therefore the size and mass of a device can be decreased to the maximum extent possible for its prescribed functional possibilities. Modern electronic devices often operate with sharp temperature differentials, so that the microcircuits must possess a high heat resistance. This condition can be satisfied if the CLTE of the glass solder, the ceramic base of the package, and metal leads of the microcircuits are all compatible with one another. Microcircuit indicators such as the maximum working temperature and the operational stability and service life are temperature dependent, and these dependences are largely contradictory. Thus, to increase the working temperature it is best to use refractory glass solders, but high sealing temperatures are a source of thermionic emission of electrons, which greatly decreases reliability, stability and service life of microcircuits. In this connection a sealing temperature of 390 – 420°C is considered to be optimal.

The most suitable glass bases meeting the indicated requirements are obtained with a lead-borate eutectic (85%[3] PbO, 15% B_2O_3) base [1 – 3]. The deformation onset temperature of the glasses synthesized in this system are $t_{d.o} = 305 – 350°C$, CLTE — $(100 – 115) \times 10^{-7}\ K^{-1}$, surface crystallization near the sealing temperature (400 – 450°C) — 1 – 15%, ρ at 150°C — to $10^{11}\ \Omega \cdot cm$ and ε — 18 – 19. With crystalline fillers added (lead titanate, zircon, β eucryptite and cordierite sitals) such glasses make it possible to obtain glass solders with sealing temperature 390 – 450°C, CLTE $(62 – 69) \times 10^{-7}\ K^{-1}$, $\rho = 10^{11} – 10^{12}\ \Omega \cdot cm$, $\varepsilon = 9 – 27$, and all other properties satisfying the requirements for glass solders used for sealing glass ceramic packages of integrated circuits [1, 2]. Unfortunately, lead and its inorganic compounds, including glass on a lead-borate base, are highly toxic. According to GOST 12.1.005–76 they belong to hazard class I with the maximum admissible concentration 0.010 – 0.005 mg/m^3. This requires that high-lead glasses be replaced with less toxic glass but with the same fusibility.

The division of glasses into low-melting and refractory is conventional. Ordinarily, glasses whose softening tempera-

[1] Scientific – Research and Industrial Enterprise for Materials Engineering, Erevan, Armenia.
[2] E-mail: geodakyan@netsys.am.

[3] Here and below — content by weight.

0361-7610/09/1112-0381

TABLE 1.

Sample of lead glasses	Content, wt.%					CLTE, 10^{-7} K^{-1}, 20 – 200°C	Temperature, °C					h, mm
	PbO	P_2O_5	ZnO	B_2O_3	other		t_{st}^*	$t_{d.o}^*$	t_g	t_{on}^{cr}	t_{max}^{cr}	
1	70.0	30.0	–	–	–	148.2	333	328	383	394	412	100**
2	61.0	39.0	–	–	–	146.2	311	320	330	381	411	100**
3	50.0	50.0	–	–	–	141.7	209	280	249	263	291	40
4	47.0	47.0	–	–	6 SiO_2	115.1	340	375	389	415	617	100**
5	47.0	47.0	–	–	6 Al_2O_3	94.2	404	446	463	–	608	100**
6	58.0	37.0	–	–	5 V_2O_5	117.2	365	–	397	533	580	14
7	49.0	49.0	2.0	–	–	133.3	290	309	322	344	504	100**
8	45.0	45.0	10.0	–	–	120.2	316	331	347	405	590	100**
9	58.0	37.0	2.7	2.3	–	125.7	345	–	385	485	522	5
10	70.0	–	10.0	10.0	10 Al_2O_3	96.3	323	335	363	No crystallization		
11	66.0	–	16.0	12.0	4 BaO, 2 TiO_2	87.2	347	381	405	422	527	22.5
12	61.6	–	20.0	12.0	2 BaO, 3.4 Nb_2O_5, 1 MnO	84.0	370	396	430	465	580	17.5
13	61.0	–	16.0	16.0	2 SiO_2, 3 Al_2O_3, 2 ZrO_2	76.2	403	428	437	647	695	17.5
14	67.0	–	14.0	14.0	2 SiO_2, 1 MgO, 1 Al_2O_3, 1 ZrO_2	81.1	390	411	417	472	515	16.0
15	62.0	–	19.0	10.0	2 SiO_2, 4 BaO, 2 TiO_2, 1 MnO	87.3	374	406	438	No crystallization		
16	62.0	–	17.0	15.0	2 SiO_2, 1 MgO, 2 Al_2O_3, 1 ZrO_2	81.0	389	412	435	577	657	26.7
17	60.0	–	5.0	14.0	5 Al_2O_3, 5 Bi_2O_3, 5 MnO_2, 5 CdO, 1 CuO	–	361	–	394	467	–	–

* Deformation onset temperature.

** The degree of surface crystallization of the glasses, % (420°C, 30 min), is presented for samples 1 – 5 and 7, 8.

ture t_g does not exceed 600°C are considered to be low-melting. The compositions, structure, and properties of low-melting glasses have been studied in detail in many monographs and articles, including [2 – 7]. We shall briefly present the results for individual groups of these glasses.

High-borate low-melting glasses as well as high-phosphate glasses are chemically unstable. Introducing PbO and B_2O_3 or P_2O_5 increases their stability. Glasses containing PbO are most common. Their softening temperature is 300 – 500°C and the CLTE is (76 – 120) × 10^{-7} K^{-1}. Glasses containing Bi_2O_3 and Tl_2O_3 have lower melting points, but their CLTEs are comparatively high — (90 – 160) × 10^{-7} K^{-1}. The softening temperature of germanate glasses is 300 – 580°C and the CLTE is (65 – 120) × 10^{-7} K^{-1}, but they exhibit low chemical stability. Introducing halides into glass appreciably lowers the softening temperature while increasing the CLTE and increasing the crystallization capacity. Of all low-melting glasses those containing ZnO have the lowest CLTE — 60 – 70 × 10^{-7} K^{-1} and glasses containing PbO have the highest chemical stability. For this reason, low-melting glasses containing lead and zinc oxides as the main components are most often used in practice.

The founding and usage properties of these glasses improve with the addition of boron anhydride. Depending on the ratio of the components, the CLTE of PbO – B_2O_3 – ZnO glasses ranges from 50 × 10^{-7} K^{-1} to 120 × 10^{-7} K^{-1}, the softening temperature ranges from 330 to 630°C, and the soldering temperature ranges from 390 to 700°C [3].

The temperature $t_{d.o}$ of vanadate glasses lies in the range 200 – 600°C and the CLTE is (600 – 250) × 10^{-7} K^{-1}. They are very "short," which makes it possible to perform soldering close to the softening temperature. V_2O_5 forms with P_2O_5, GeO_2, TeO_2, BaO, and PbO binary or ternary low-temperature eutectic mixtures, which are stable against crystallization.

Vanadate glasses are high-resistance semiconductors. In the system V_2O_5 – P_2O_5 – CdO ρ of the glasses lies in the range 10^5 – 10^{12} Ω · cm depending on the ratio of the components.

Among all inorganic glasses the chalcogenide glasses have the lowest melting points. The softening temperature of these glasses ranges from – 60 to + 450°C depending on the composition. In the main groups from IV to VI in the periodic table of the elements t_g decreases with increasing atomic

mass of the chalcogenides (S > Se > Te, P > As > Sb, Si > Ge > Sn). The CLTE of these glasses is very high — $(168 - 425) \times 10^{-7}\,K^{-1}$. The volatility of chalcogenide glasses is also high, which predetermines their use in electronics, mainly as protective and passivating coatings for microcircuits, recording layers of photothermoplastic carriers of information, and so on [7].

It should be noted that many glass-forming and modifying oxides of low-melting glasses are just as safe as PbO (CdO, CeO_2, Tl_2O_3 — hazard class I; V_2O_5, TeO_2, ZnO, P_2O_5, BaO, SrO, Bi_2O_3, fluorides are class II; Sb_2O_3, GeO_2, B_2O_3 — are class III; all other oxides — class IV). So that to select less dangerous glasses the content of not only PbO but also the components which belong to hazard class I would have to be limited.

In the present work we investigate the possibility of synthesizing low-melting lead, vanadate, and tellurite glasses with total content of hazard class I components not exceeding 70%.

Pure, analytically pure, and chemically pure materials were used. The mixes were prepared by dry mixing of the components in a porcelain mortar or in a laboratory V-shaped mixer with approximately 20 ml capacity. The glasses were made in platinum or corundum crucibles with 50 – 300 ml capacity in an electric muffle furnace with carborundum heaters. Depending on the glass composition the glass-making temperature was 900 – 1200°C and the process time was 30 – 60 min. Extraction was performed by pouring the glass melt onto a steel plate, and comminution was performed in a porcelain ball mill or an agate mortar (in the case of small portions) by the dry method.

Preliminary glass extraction was done from the surface of crystallization of the melts poured onto the steel plate. Glass with volume or continuous surface crystallization was scrapped. The scrapped glass was investigated by means of differential thermal analysis (Inventor's Certificate No. 999760). The onset temperature, maximum rate, and completion of the transformation transition of the glasses were determined by DTA: (t_{st}, $t_{max} = t_g$, and t_f); onset t_{on}^{cr}, maximum rate t_{max}^{cr}, and t_{end}^{cr} end of crystallization as well as the height h of the crystallization peak. The glasses monitored by DTA were checked dilatometrically (DKV-4, RF). In a number of packages the surface crystallization of samples obtained by pressing powders followed by fusion at 400 and 425°C with 20 – 60 min soaking) was also determined (POLAM R-312 microscope, RF).

More than 500 glass compositions were investigated. The most promising ones are presented in Tables 1 – 3.

It follows from the data in Table 1 that with respect to the CLTE, fusibility (t_{st} and $t_{d.o}$), and crystallization capacity (degree of surface crystallization) lead glasses containing no more than 70% PbO are not nearly as good as lead-borate eutectic glasses, so that they cannot be used in glass solder compositions with sealing temperatures 390 – 420°C. However, because of their low CLTEs some PbO – ZnO – B_2O_3 glasses, probably without crystalline additives, could be used in thick-film technology for producing hybrid integrated circuits based on float glass (CLTE $80 \times 10^{-7}\,K^{-1}$).

TABLE 2.

Sample of vanadate glasses	Content, wt.%					t_{st}, °C	t_g, °C	t_{on}^{cr}, °C
	V_2O_5	P_2O_5	ZnO	B_2O_3	other			
1	80.0	20.0	–	–	–	254	294	342
2	60.0	40.0	–	–	–	304	344	514
3	65.0	25.0	–	–	10 CdO	352	389	528
4	65.0	25.0	–	–	10 BaO	294	350	449
5	66.7	28.6	–	–	4.7 GeO_2	291	362	476
6	63.4	34.1	–	–	2.5 Al_2O_3	321	378	478
7	70.0	25.0	–	–	5 PbO	227	266	–
8	60.0	15.0	–	–	25 PbO	290	342	429
9	63.4	34.1	2.5	–	–	323	387	508
10	65.1	27.9	7.0	–	–	290	340	433
11	65.1	27.9	4.6	–	2.3 La_2O_3	283	353	500
12	65.1	27.9	4.6	–	2.3 TiO_2	305	348	512
13	65.1	27.9	2.4	–	4.6 TeO_2	278	344	455
14	52.8	22.6	1.9	–	22.7 TeO_2	290	366	505
15	70.0	–	30.0	–	–	250	285	300
16	68.0	–	27.0	5.0	–	254	290	290
17	60.0	–	27.0	13.0	–	238	282	282
18	70.0	–	–	15.0	15 CdO	245	275	283
19	50.0	–	–	25.0	25 CdO	255	316	320
20	65.1	27.9	4.6	2.3	–	284	331	505

Laboratory studies of the indicated glasses as protective coatings based on float-glass using different binding materials showed that the best results are obtained with the glasses 14 and 16 using a 15% water solution of ethylene glycol (10%) with 300 μm thick layer, drying (140°C, 10 min), firing (420°C, 30 min), and fusing (480°C, 10 min). According to the results obtained, the glass 14 is recommended for use as protective, resistive, and semiconductor pastes intended to deposition on float-glass and as solder for joining glass – glass – ceramic – ceramic – metal – metal with CLTE about $80 \times 10^{-7}\,K^{-1}$.

Vanadate glasses (see Table 2) are more fusible than lead glasses, but they possess high crystallization capacity. For this reason only the crystallization onset temperatures of the glasses are presented in Table 2 and are close to the softening temperature for most of the glasses. It is known that these glasses also possess a comparatively low CLTE [6]. Therefore one would expect that glass solders suitable for sealing glass ceramic packages for integrated circuits can be obtained on the basis of vanadate glasses with a quite large difference $t_{on}^{cr} - t_g$ without crystallization additives or with large additions. To this end the glasses 12 and 20 were chosen. They were additionally investigated by dilatometric methods and tested in the course of fabrication and sealing of the microcircuit packages. Their CLTE was $70 \times 10^{-7}\,K^{-1}$,

TABLE 3.

Sample of tellurite glasses	Content, wt.%					Dilatometric properties		log ρ at 150°C	Dielectric properties at 1 MHz (20°C)	
	TeO_2	PbO	Bi_2O_3	V_2O_5	other	CLTE, 10^{-7} K^{-1}, 20 – 200°C	$t_{d.o}$, °C		ε	tan δ × 10^4
1	55.0	30.0	–	–	15 BaO	204.5	305	9.80	24.0	15.3
2	50.0	34.0	1.0	–	15 BaO	196.2	282	9.90	24.3	15.2
3	49.0	31.5	8.0	10.5	1 CdO	174.3	288	10.70	23.6	14.8
4	40.5	35.0	8.5	16.0	–	176.4	284	9.70	24.5	15.6
5	40.5	35.0	8.5	15.0	1 SrO	181.7	303	9.70	24.2	15.5
6	40.5	35.0	8.5	9.0	6 BaO, 1 SrO	192.0	302	10.01	24.8	15.3

which is comparable to the CLTE of the ceramic VK 94-1 ($65 \pm 5 \times 10^{-7}$ K^{-1}).

The tests showed that for dry deposition of the glasses on ceramic at 410 – 420°C a normally fused and vitrified coating is formed. The bonding of the glass with the ceramic is good. However, the glasses were found to be incompatible with the binder used in practice (3% solution of ethylcellulose in terpineol with dibutylphthalate).

The tellurite glasses (see Table 3) had the lowest crystallization capacity of all glasses studied. They did not crystallize not only in the dynamic heating regime but also with long (up to 60 min) soaking at 350, 400, and 450°C. These glasses have quite low melting temperatures, but they possess high CLTE, comparable to that of aluminum metal. This made it possible to use the glasses obtained without additives to fabricate and seal aluminum packages for large integrated circuits. Practically all tellurite glasses presented in Table 3 were used for this.

The glasses 4 and 5 were chosen. They were deposited on an anodized surface of aluminum and on an enameled surface (composition, %: 33 SiO_2, 21 TiO_2, 2 Al_2O_3, 7 B_2O_3, 1 CaO, 1 MgO, 1 K_2O, 2 Na_2O, and 4 Li_2O; enameling temperature 560 – 570°C). The glass solders were deposited by the dry method (hot printing) and by printing using stencils and pastes based on ethyl alcohol.

Copper and 42N alloy removal output frames melted on the bases of the packages at 360°C (30 sec) were investigated. The sealing temperature of the packages was 330 – 340°C and the soaking time was 5 min. The sealed packages failed tests for large and small leaks. The glass solder seam possesses high porosity, high degree of cracking, and low mechanical strength, which was probably due to technological omissions and a sharp change of the CLTE of aluminum in the temperature range 120 – 200°C. Nonetheless, the search for compositions of tellurite glasses and the technological particulars of the preparation and deposition of pastes based on them for fabricating and sealing aluminum and, possibly, copper packages of large integrated circuits should continue.

In summary, it is impossible to find in systems with comparatively low content of PbO and other toxic oxides a full-fledged replacement with glasses in the lead-borate eutectic used as a glass base in glass solder compositions for sealing glass ceramic packages of integrated microcircuits at temperatures 390 – 420°C. Nonetheless, vanadate based glasses (V_2O_5 – P_2O_5 – ZnO) without crystalline additives and with appropriate methods of deposition and an organic binder in the pastes can probably be used for fabrication and low-temperature sealing of microcircuit packages. Definite glasses from the systems PbO – ZnO – B_2O_3 and TeO_2 – PbO – Bi_2O_3 – V_2O_5 can be used with the appropriate paste compositions and deposition methods to obtain layers with different functions on the basis of float-glass in the fabrication and low-temperature sealing of metal packages of large integrated circuits.

REFERENCES

1. I. W. Donald, "Preparation and chemistry of glass and glass ceramic-to-metal seals and coatings," *Mater. Sci.*, **28**, 2871 – 2886 (1993).
2. D. A. Geodakyan, B. V. Petrosyan, and K. D. Geodakyan, "Design and synthesis of fusible glass solders with prescribed properties," *Steklo Keram.*, No. 9, 27 – 33 (2007); D. A. Geodakyan, B. V. Petrosyan, and K. D. Geodakyan, "Design and synthesis of fusible glass solders with previously assigned properties," *Glass Ceram.*, **64**(9 – 10), 326 – 332 (2007).
3. D. A. Geodakyan, B. V. Petrosyan, and K. D. Geodakyan, "Low melting lead-containing glasses," *Izv. Nats. Akad. Nauk Armenii*, **3**, 441 – 447 (2007).
4. V. Yu. Vasil'ev, "Thin layers of borophosphorosilicate glass in silicon microelectronics technology. Part 1. Deposition from the gas phase and properties of glass layers," *Mikroelektronika*, **33**(5), 334 – 351 (2004).
5. V. Yu. Vasil'ev, "Thin layers of borophosphorosilicate glass in silicon microelectronics technology. Part 2. Structure of glasses and their application in technology," *Mikroelektronika*, **34**(2), 83 – 97 (2005).
6. V. Dima, P. Balta, M. Eftimie, and V. Ispas, "Low melting glasses in the system SnF_2 – $SnCl_2$ – PbO – P_2O_5," *Optoelectron. Advanced Mater.*, **8**(6), 2126 – 2128 (2006).
7. V. G. Dzhavadyan, M. Yu. Abovyan, D. A. Geodakyan, and R. M. Oganesyan, "Glasses and glass compositions for passivating and sealing of semiconductor devices," *Vestn. Stroitelei Armenii*, No. 2, 23 – 25 (2001).